



## Synthesis of Nitrogen Doped Titanium Dioxide (TiO<sub>2</sub>) and its Photocatalytic Performance for the Degradation of Indigo Carmine Dye

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### Abstract

Nitrogen (N) doped TiO<sub>2</sub> were synthesized by thermal decomposition of the mixture of TiO<sub>2</sub> and urea at 500 C. Optical and structural properties of N doped TiO<sub>2</sub> were investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, UV-visible diffusion reflectance spectroscopy (UV-DRS) and scanning electron microscopic (SEM) techniques. XRD showed that anatase phase was converted into rutile phase while increasing the content of urea. FTIR studies revealed that number of hydroxyl group on TiO<sub>2</sub> surface decreases with increasing the concentration of nitrogen. SEM studies were carried out for the morphological features and size of TiO<sub>2</sub> particles. DRS data showed a red shift in absorption edge and band gap become narrower while increasing the concentration of nitrogen. The photocatalytic activity was evaluated for photodegradation of indigo carmine dye under UV light irradiation.

**Keywords :** Indigo carmine dye ; Nitrogen ; Photo catalytic activity ; Titanium dioxide.

### 1. INTRODUCTION

Heterogeneous photocatalysis has emerged as an efficient technology to purify air and water (Hoffmann et al. 1995; Fujishima et al. 2008; Vohra et al. 2006). TiO<sub>2</sub> was the most widely used photocatalyst because of its good activity, chemical stability, commercial availability, and inexpensiveness (Xu et al. 2008). TiO<sub>2</sub> occurs mainly in three crystalline phases namely anatase, rutile and brookite, and rutile is the thermodynamically most stable phase. They differ in their physical properties, such as refractive index, dielectric constant, chemical and photochemical reactivity. It is well known that the photocatalytic activity of TiO<sub>2</sub> is intimately related with its crystal structure (Ohtani et al. 1997). While TiO<sub>2</sub> in anatase phase has high photocatalyst activity, the rutile TiO<sub>2</sub> shows no appreciable activity. However, the large band gap of TiO<sub>2</sub> (3.2 eV) restricts its

photocatalytic applications to the UV range. Therefore, solar light cannot be fully utilized. Therefore, improving the optical properties of TiO<sub>2</sub> by modifying its band gap is necessary.

Doping is one of the typical approaches to extend the spectral response of a wide band gap semiconductor to visible light, where some metal ions can be used as a dopant (Jeon et al. 2000; Fuerte et al. 2002; Tian et al. 2009). However, metal doping has several drawbacks. The doped materials have been shown to suffer from thermal stability (Choi et al. 1994), and the metal centres act as electron traps, which reduces the photocatalytic efficiency. Alternatively, some groups reported results on the doping of non-metal elements such as B, C, N, F and S on TiO<sub>2</sub> have shown the desired electron-hole trapping and band gap narrowing and the results have been successfully achieved rather than metal ions (Mozia et al. 2005; Irie et al. 2003; Xu et al. 2009; Wang et al. 2008; Yu et al. 2002). The anion-doped TiO<sub>2</sub> photocatalysts showed good

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photocatalytic activity under visible light. Among the non-metal dopant, N is one of material that enhance the photoresponding range into visible light. Horst et al. 2007 reported that band gap energy of  $\text{TiO}_2$  can be reduced from 3.18 to 2.20 eV by nitrogen incorporation. Mekprasart et al. 2011 observed that the photocatalytic degradation of Rhodamine B solution was enhanced by N doped  $\text{TiO}_2$ . Jing Li et al 2010 reported that the significant visible light response and strong increase of photocurrent under UV and visible range were obtained by N-doped  $\text{TiO}_2$ . Cheng et.al 2012 proposed that the formation mechanism of N doped  $\text{TiO}_2$  and proved that photocatalytic activity of phenol was improved by N doped  $\text{TiO}_2$ . Bangkedphol et.al 2010 reported on the improvement of photocatalytic degradation of tributyltin under natural light by using N-doped  $\text{TiO}_2$ . Chainrang et.al 2011 reported that N doped  $\text{TiO}_2$  shows highest photocatalytic activity. It was found that photocatalytic activity increases in N doped  $\text{TiO}_2$  was due to nitrogen atoms filled into the lattice of  $\text{TiO}_2$  and the absorption edge shifting to visible light region.

Indigo carmine (IC) dye, molecular formula  $\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ , is one of the oldest dyes and still one of the most important used. It mainly used as textile colouring agent and additive in pharmaceutical tablets and capsules as well as in confectionery items, indigo carmine is also used for medical diagnostic purposes. The indigo carmine is considered as highly toxic indigoid class of dye. It cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva (Barka et al. 2008). The consumption of the dye can also prove fatal, as it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity (Jenkins 1978). It has also been established that the dye leads to tumours at the site of application (Yoshida et al. 1971). Thus various attempts have been made for the removal of indigo carmine from water and wastewater. The photocatalytic treatment is a more attractive technique for the removal of soluble organic compounds. So in present study, N doped  $\text{TiO}_2$  was synthesized and photodegradation of indigo carmine dye was studied.

## 2. EXPERIMENTAL

Initially analar grade  $\text{TiO}_2$  was powdered and heated to at 500°C for 5 hours in muffle furnace. In another

series, nitrogen (N) doped  $\text{TiO}_2$  was synthesized by mixing analar grade 1M of  $\text{TiO}_2$  and different concentration of urea (1M to 4M), which represented as 1:1, 1:2, 1:3, 1:4 N doped  $\text{TiO}_2$ . Mixed salt was grained to powder it was heated at 500°C for 5 hours in muffle furnace. The synthesized product was subjected to different characterization.

The samples was subjected to the X-ray powder diffraction (XRD) analysis on a Bruker AXS D8 advanced with monochromatic  $\text{CuK}\alpha$  – radiation ( $\lambda = 1.5406\text{\AA}$ ). The crystallite size of the powders was determined by Scherer equation. FT-IR spectra were obtained using a Perkin-Elmer grating infrared spectrometer. The morphology of samples was characterized using a JEOL JSM-6390LV scanning electron microscope. UV-vis adsorption spectra were measured on a TU-1900 single-beam UV-vis spectrophotometer. The photocatalytic activities of pure  $\text{TiO}_2$  and N doped  $\text{TiO}_2$  nanoparticles was measured by the degradation of indigo carmine dye under UV irradiation.

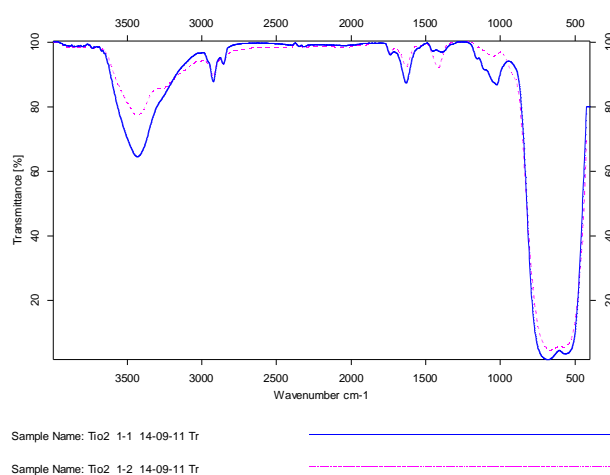


Fig. 1 : FTIR spectra of (a) 1:1 and (b) 1:2 N doped  $\text{TiO}_2$

## 3. RESULT AND DISCUSSION

### 3.1 FTIR analysis of pure $\text{TiO}_2$ and N- doped $\text{TiO}_2$

The FTIR spectra were recorded in the range 400-4000  $\text{cm}^{-1}$ . FT-IR spectra of 1:1 and 1:2 N-doped  $\text{TiO}_2$  samples were shown in Fig. 1 respectively. The absorption peaks

at 3431, 2925 and 2856  $\text{cm}^{-1}$  were assigned to the OH species (Kamal et al. 1997). The absorption peak at 1633  $\text{cm}^{-1}$  belongs to the Ti–O structure (Navio et al. 1996). The FT-IR characterization confirms the substitution of crystal lattice O to N species and the formation of N–Ti–O bond. The strong absorption band in the region 480 to 700  $\text{cm}^{-1}$  in the spectra of 1:1 N-doped  $\text{TiO}_2$  and 1:2 N-doped  $\text{TiO}_2$  has been assigned to the -Ti-O- stretching (Wang et al. 2009). The peaks at 1417 and 1050  $\text{cm}^{-1}$  could be attributed to the nitrogen atoms embedded in the  $\text{TiO}_2$  network (Shanmugasundaram et al. 2004; Li et al. 2006). These results clearly demonstrated that the nitrogen has been incorporated into the  $\text{TiO}_2$  lattice. The nitridation occurred by replacing the oxygen atom in the  $\text{TiO}_2$  with the nitrogen atom in the urea molecule, resulting in the formation of the O–Ti–N species. The FT-IR investigation confirms that 1:2 N-doped  $\text{TiO}_2$  has a lower amount of surface OH groups than 1:1 N-doped  $\text{TiO}_2$ . The hydroxyl groups on the surface contributes to the improvement of the photocatalytic activity by their interactions with photogenerated holes giving better charge transfer, which inhibits the recombination of electron–hole pairs.

### 3.2 Powder XRD analysis of N doped $\text{TiO}_2$

Powder XRD pattern of N-doped  $\text{TiO}_2$  particles was shown in Fig. 2. XRD patterns of 1:1 N-doped  $\text{TiO}_2$  (Fig. 2(a)) shows that the material was in pure anatase phase, and the average crystallite size of the material calculated from the Full Width Half Maximum (FWHM) of (1 0 1) diffraction using Debye–Scherrer was found to be 127 nm.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where D is the average crystallite size, k is a shape constant, which is equal to 0.9 (assuming the particles are spherical);  $\lambda$  is the wavelength of X-ray and  $\beta$  is the FWHM in radians and  $\theta$  is the Bragg angle.

In the XRD pattern of 1:2 N doped  $\text{TiO}_2$  (Fig. 2(b)) there is a weak peak at  $28.3^\circ$  indicates the presence of rutile phase  $\text{TiO}_2$ . The transformation of  $\text{TiO}_2$  from

anatase to rutile phase usually occurs on heating anatase  $\text{TiO}_2$  above  $600^\circ\text{C}$ . Thermal decomposition of urea is also an exothermic reaction, hence the heat liberated might increase the temperature around the crucible beyond the furnace temperature ( $500^\circ\text{C}$ ), and thus the anatase to rutile phase transformation was observed in high urea content 1:2 N doped  $\text{TiO}_2$ . The conversion of anatase phase to rutile phase on nitration of  $\text{TiO}_2$  with urea was also reported Rattanakam et.al 2009. The crystallite size of the 1:2 N doped  $\text{TiO}_2$  was also 127 nm, this shows that the doping of nitrogen does not affect the size of the  $\text{TiO}_2$ . The crystallinity

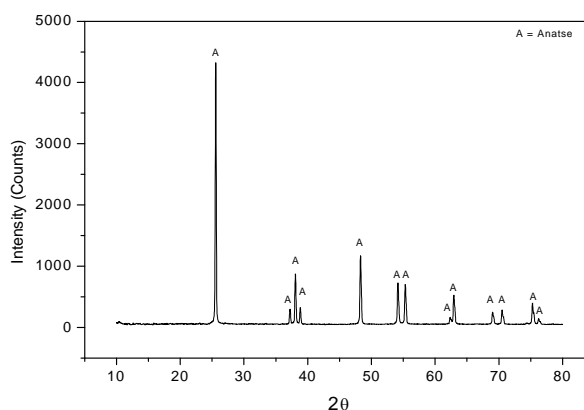


Fig. 2(a) : Powder XRD pattern of 1 : 1 N doped  $\text{TiO}_2$

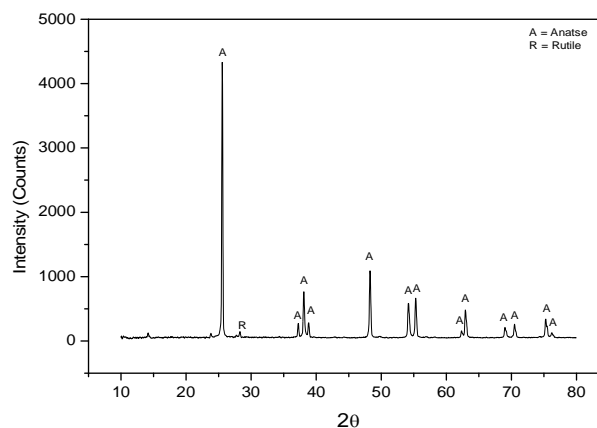
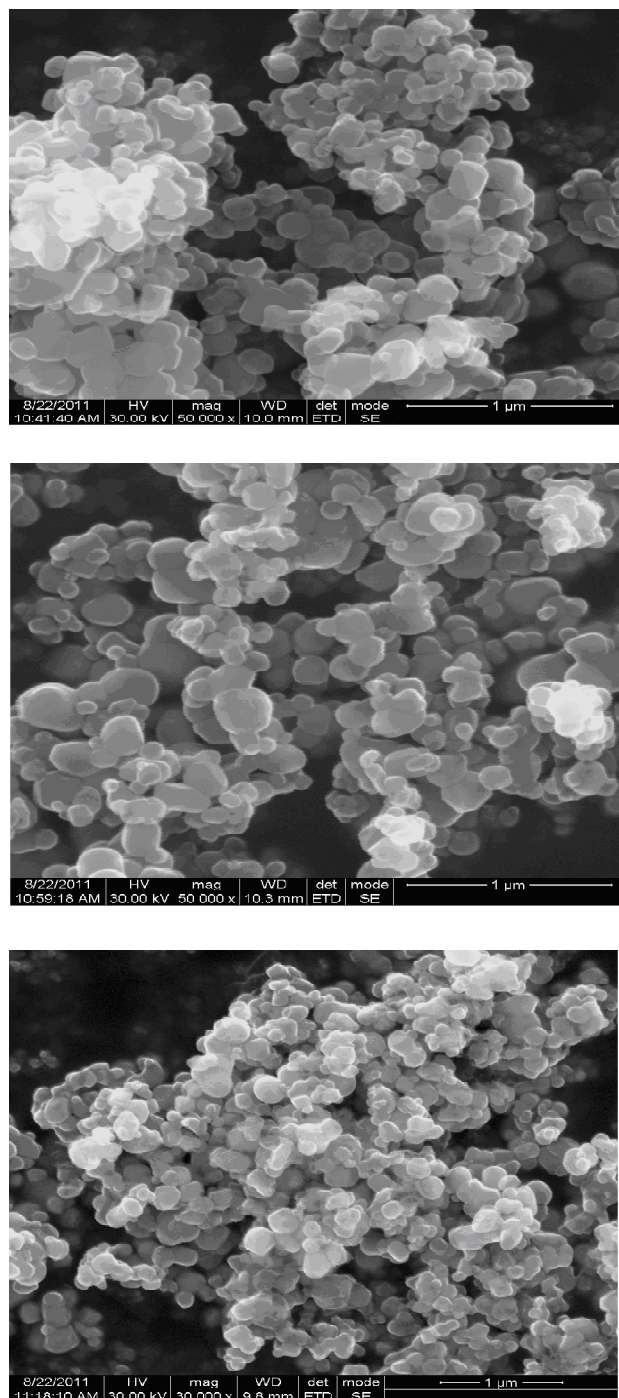


Fig. 2(b) : Powder XRD pattern of 1 : 2 N doped  $\text{TiO}_2$

is high which was beneficial to the enhancement of photocatalytic activity N doped sample exhibited typical structure of  $\text{TiO}_2$  crystal without any detectable dopant

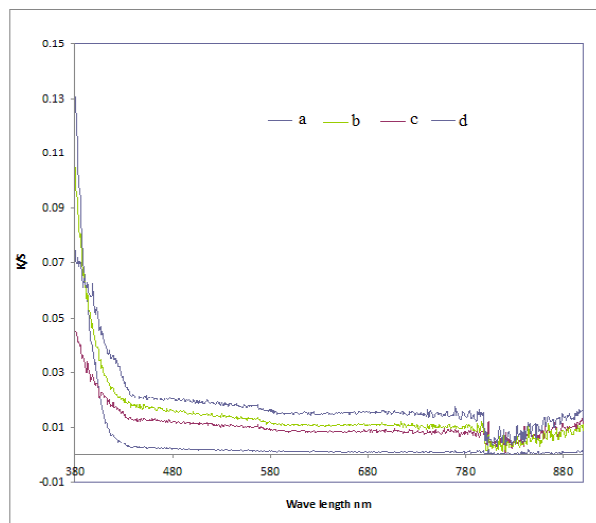


**Fig. 3 :** SEM image of (a)  $\text{TiO}_2$ ; (b) 1:1 N-doped  $\text{TiO}_2$ ; (c) 1:2 N-doped  $\text{TiO}_2$

any detectable dopant related peaks. The reason could be due to the fact that, nitrogen species have moved into either the interstitial positions or the substitutional sites of the  $\text{TiO}_2$  crystal structure.

### 3.3 SEM analysis

The Scanning Electron Microscopy images (Fig.3) show that all the three photocatalysts ( $\text{TiO}_2$ , 1:1 N-doped  $\text{TiO}_2$  and 1:2 N-doped  $\text{TiO}_2$ ) consist of irregular agglomerated nanoparticles of size ranging from 70 to 150 nm. The images also reveals that the morphology and size of the particle were not changed on incorporation of nitrogen on  $\text{TiO}_2$  by treatment with urea at 500 °C. The morphology of the  $\text{TiO}_2$  particles was not altered on nitrogen doping due to the comparable atomic size of nitrogen atom with oxygen.



**Fig. 4 :** UV-DRS spectra of  $\text{TiO}_2$  and N doped  $\text{TiO}_2$

### 3.4 UV-Visible diffuse reflectance spectral analysis

Diffuse reflectance spectroscopy was used to determine the absorption shift and the bandgap energy of all the samples. The UV-vis diffuse reflectance spectra of samples with different N contents are depicted in Fig. 4. Reflectance was converted to  $F(R)$  values according to the Kubelka-Munk theory. As it can be seen in Fig. 4,

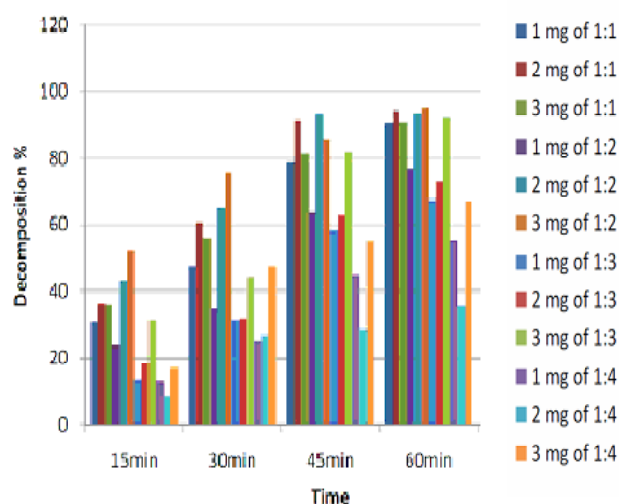
N-doped TiO<sub>2</sub> samples show a strong absorption in the visible range, demonstrating a red shift in the band gap transition of the samples. The absorption shift to the higher wavelength became prominent as the concentration of N dopant was increased. The band gap of the samples was determined by the equation

$$E_g = 1239.8/\lambda$$

where  $E_g$  is the band gap (eV) and  $\lambda$  (nm) is the wavelength of the absorption edge in the spectrum. The sample showed an absorption edge at 384 (TiO<sub>2</sub>), 394 (1:1 N doped TiO<sub>2</sub>), 403 (1:2 N doped TiO<sub>2</sub>), and 430 (1:3 N doped TiO<sub>2</sub>), corresponding to the band gap 3.23 eV (TiO<sub>2</sub>), 3.15 eV (1:1 N doped TiO<sub>2</sub>), 3.08 eV (1:2 N doped TiO<sub>2</sub>), and 2.89 eV (1:3 N doped TiO<sub>2</sub>). In overall the band gap of TiO<sub>2</sub> narrowed from 3.23 eV to 2.89 eV on doping of nitrogen. This narrowing of band gap on doping may be due to the mixing of N 2p orbitals with O 2p orbitals.

### 3.5 Photocatalytic activity of N doped TiO<sub>2</sub>

The photocatalytic activities of N doped TiO<sub>2</sub> was measured by the degradation of indigo carmine aqueous solution under UV irradiation was shown in Fig.5. In 1mg



**Fig. 5 : Photodegradation of IC dye in presence of N doped TiO<sub>2</sub> under UV irradiation**

of dye solution, different nitrogen concentration in TiO<sub>2</sub> was added and irradiated with UV lamp to provide excitation to TiO<sub>2</sub>. The experiment demonstrated that the observed photocatalytic activity was high in 1:1 N doped TiO<sub>2</sub> and then decreased by further increasing the content of N ion. This result implies there was an optimum molar content of N ion at 1M. When TiO<sub>2</sub> was doped with the appropriate content of N, N impurity energy level would be a separation centre, and thus enhance the photocatalytic activity of TiO<sub>2</sub>. But when the content of N ion was higher than its optimal level, a large quantity of N cannot diffuse into the TiO<sub>2</sub> lattice, but deposit on the surface of TiO<sub>2</sub> particles. Their existence on the particle surface of TiO<sub>2</sub> lessens the specific area of TiO<sub>2</sub>, impedes the adsorption of reactant and thus inhibits the photocatalytic activity. Further increasing the content also can promote the transformation of anatase to rutile, which has little photocatalytic activity. It is well known that the activity of anatase phase of TiO<sub>2</sub> in the degradation of various pollutants is in general much higher than that of rutile (Carp et al. 2004; Augustynski et al. 1993; Akurati et al. 2006).

The rate of photodegradation of indigo carmine dye was studied by varying the dye concentration from 1mg/mL to 3mg/mL. It observed that 2mg/mL of TiO<sub>2</sub> was the optimum dose for efficient degradation of indigo carmine dye. Because for a fixed concentration of active sites remaining the same, the number of substrate ions accommodated in the interlayer space increases so that the degradation decreases. This may be due to the fact that with increase in initial concentration of the dye, more dye molecules are also adsorbed on the surface of TiO<sub>2</sub>. Thus, increase in the number of substrate ions accommodating in inter layer spacing inhibit the action of catalyst which thereby decreases the reactive OH and O<sub>2</sub><sup>-</sup> free radicals attacking the dye molecules and photodegradation efficiency (Shrivastava et al. 2011).

The FTIR study reveals that 1:1 N doped TiO<sub>2</sub> has large amount of hydroxyl group on the surface. The hydroxyl groups on the particles surface contributes to the improvement of the photocatalytic activity by their interactions with photo generated holes giving better charge transfer, which inhibits the recombination of electron-hole pairs. The observed higher photocatalytic activity for 1:1 N doped TiO<sub>2</sub> was further supported by FTIR study.

#### 4. CONCLUSION

Nitrogen (N) doped  $\text{TiO}_2$  were synthesized by thermal decomposition of the mixture of  $\text{TiO}_2$  and urea at 500 C. XRD, FTIR, and UV- DRS studies confirmed that the nitrogen was incorporated in  $\text{TiO}_2$ . SEM image reveals that the morphology and size of the particle were not changed on incorporation of nitrogen on  $\text{TiO}_2$ . DRS data showed a red shift in absorption edge and band gap become narrower while increasing the concentration of nitrogen. According to our results, the photocatalytic activity was not depending on narrowing of band gap but on phase of  $\text{TiO}_2$ . The anatase phase 1:1 N doped  $\text{TiO}_2$  shows higher photocatalytic activity than other samples. Finally 1:1 N doped  $\text{TiO}_2$  catalysts are potential to be used as photocatalyst and will be a good candidate for water purification.

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